1) Publication number:

0 304 143 Δ1

② EUROPEAN PATENT APPLICATION

2 Application number: 88303631.1

(2) Date of filing: 21.04.88

(a) Int. Cl.4: C02F 3/10 , C12N 11/08 , C08F 20/60 , C08F 20/34 , C08L 33/14

© Priority: 19.08.87 JP 204246/87

Date of publication of application:22.02.89 Bulletin 89/08

Designated Contracting States:
 DE ES FR GB NL

Applicant: KYORITSU YUKI CO. LTD. 13-15 Ginza 7-chome Chuo-ku Tokyo(JP)

2 Inventor: Fukushima Reizou 8-38, 2-chome, Shimomachiya Chigasaki-shi, Kanagawa-ken(JP) Inventor: Aoyama Kiyoshi 225-3, Omagari, Samukawa-machi Kouza-gun, Kanagawa-ken(JP)

Representative: Pendlebury, Anthony et al Page, White & Farrer 5 Plough Place New Fetter Lane London EC4A 1HY(GB)

Water-absorptive resin for microbial carrier.

A water-absorptive resin, which comprises a cationic crosslinked polymer comprising at least 10% by weight of cationic monomer unit(s) and containing a magnetic material therein, is used as a microbial carrier in a fluidized bed biodisposer. This water-absorptive resin can serve as a microbial carrier when merely introduced into a liquor containing a microorganism. Thus seeding can be readily carried out by using the same. Further the carrier is magnetic and thus can be readily recovered. In addition, the specific gravity of the resultant polymer gel, i.e. the resin which has absorbed water, and acting as the carrier, is closely similar to that of the filtrate. Therefore the polymer gel can be fluidized by simply stirring the same slightly by, for example, air diffusion.

EP 0 304 143 A1

WATER-ABSORPTIVE RESIN FOR MICROBIAL CARRIER

This invention relates to a water-absorptive resin available as a microbial carrier in a fluidized bed biodisposer for treating, for example, organic waste water.

There has been known a process wherein microorganisms are incorporated into a polymer gel carrier to thereby prevent the effusion thereof from a system. Examples of conventional polymer gels employed in these bioreactors include polyacrylamide, carrageenan and agarose ($[C_{12}H \cdot 4O_5(OH)_4]_n$).

There has been further known a process wherein a microorganism is incorporated into an agarose gel containing a magnetic material for use in a microbial reaction such as methane fermentation (cf. Japanese Patent Laid-Open No. 257180/1986).

However such a bioreactor is disadvantageous because of the low efficiency caused by the slow migration of nutrients and waste matters of the incorporated microorganism in the polymer gel. In addition, the incorporation of the microorganism into the gel requires a complicated procedure. Further this bioreactor should be prepared immediately before the use since it can not withstand prolonged storage. Furthermore the microorganism, being fixed in the gel, can not be renewed and thus dead cells remain in the carrier, which might inhibit the fixation of the microorganism upon prolonged operation to thereby lower the efficiency of the bioreactor. Accordingly there is a problem to be solved relating to a fluidized bed biodisposer, namely, how to efficiently stir the carrier and how to efficiently recover the carrier and replace the same with a fresh one at appropriate intervals.

It is an object of the present invention to solve the problem described above by using an acrylic cationic resin, which has a high water-absorptivity and contains a magnetic material, in a state of absorbing water as a microbial carrier for fixing a microorganism in a fluidized bed biodisposer.

It is another object of the present invention to provide a water-absorptive resin for a microbial carrier. When the water-absorptive resin as described above is introduced into a waste water as a carrier in a fluidized bed biodisposer, it would absorb a large amount of water to thereby give a cationic polymer gel comprising the water-absorbing resin containing a magnetic material. A microorganism is tightly fixed on the surface of the gel, i.e., the carrier and grows thereon. Since the microorganism layer thus formed is in direct contact with the organic waste water which is a nutritional source therefor, the microorganism can rapidly absorb nutrients and excrete waste matters.

It is still another object of the present invention to provide a water-absorptive resin for a microbial carrier in a fluidized bed biodisposer wherein a microorganism in waste water are successively renewed and thus a highly active microorganism is continuously fixed on the surface of a water-absorbing resin, i.e., the carrier.

It is still another object of the present invention to provide a water-absorptive resin for a microbial carrier in a fluidized bed biodisposer wherein the water-absorptive resin gel absorbing a large amount of waste water has nearly the same specific gravity as that of the waste water, which makes it possible to readily maintain the water-absorbing resin carrier in the waste water in a fluidized state by slightly stirring the same in the waste water with, for example, the air from a diffuser or methane gas.

It is still another object of the present invention to provide a water-absorptive resin for a microbial carrier in a fluidized bed biodisposer wherein said water-absorptive resin in a state of absorbing water, i.e., the carrier contains a magnetic material and thus can be readily recovered from the treated waste water by using a magnet.

It is still another object of the present invention to provide a water-absorptive resin for a microbial carrier in a fluidized bed biodisposer characterized in that said water-absorptive resin would exert a remarkable effect as a microbial carrier when merely introduced into water containing a microorganism, that seeding can be readily carried out, that said carrier containing a magnetic material can be readily recovered, and that the polymer gel can be fluidized by slightly stirring through, for example, air diffusion since the water-absorbing resin, i.e., the polymer gel has nearly the same specific gravity as that of the water to be treated.

It is still another object of the present invention to provide a water-absorptive resin for a microbial carrier in a fluidized bed biodisposer which can stably carry a high load compared with a conventional activated sludge process or an anaerobic methane fermentation process utilizing no distinct carrier.

In the present invention, an acrylic cationic resin of a high water-absorptivity is used as a microbial carrier in a fluidized bed biodisposer.

According to the present invention there is provided a water-absorptive resin for a microbial carrier in a fluidized bed biodisposer wherein a magnetic material is incorporated in a cationic crosslinked polymer comprising at least 10% by weight of of a cationic monomer unit(s) of the following formula:

$$-CH_{2} \xrightarrow{\stackrel{R}{\downarrow} 1} {\stackrel{R}{\downarrow} 2} {\stackrel{R}{\downarrow} 2} {\stackrel{C}{\downarrow} -A-B-N} \xrightarrow{\stackrel{R}{\downarrow} -R_{4}} X^{\bigcirc}$$

$$(I)$$

wherein A represents an oxygen atom or an NH group,

10 B represents a C₂H₄, C₃H₅ or CH₂CH(OH)CH₂ group,

R₁ represents a hydrogen atom or a methyl group,

R₂ and R₃ each independently represent a methyl or ethyl group,

R₄ represents a hydrogen atom or a methyl, ethyl, benzyl or 3-chloro-2-hydroxypropyl group, and

X⁻ represents an anion.

When introduced into a fluidized bed biodisposer, the water-absorptive resin of the present invention would absorb the water to be treated. Thus the cationic crosslinked polymer would absorb water 10 times by weight, on a dry basis, as much as the polymer per se to thereby give a cationic polymer gel containing a magnetic material. Then a microorganism is tightly fixed onto the surface of the polymer gel and grows thereon.

A crosslinked polymer comprising at least 10% by weight of acrylic water-soluble monomer unit(s) is available as the water-absorptive resin for the microbial carrier of a fluidized bed biodisposer of the present invention, namely, as the cationic resin of a high water-absorptivity available in achieving the abovementioned objects. Such a crosslinked polymer may be prepared by copolymerizing said monomer(s) with a divinyl compound or by reacting a water-soluble cationic polymer with a polyfunctional compound to thereby form crosslinkages. Examples of the acrylic water-soluble cationic monomer, available in the preparation of the polymer gel include tertiary amine salts and/or quaternary ammonium salts of dial-kylaminoalkyl (meth) acrylate and dialkylaminoalkyl(meth) acrylamide. A tertiary amine may be quaternarized by using dimethyl sulfate, diethyl sulfate, methyl chloride, benzyl chloride or epichlorohydrin. Either a homopolymer of one of these cationic monomers or a copolymer thereof may be employed. In addition, a water-soluble nonionic monomer such as (meth)acrylamide may be copolymerized therewith at a ratio of 90% by weight or less based on the total monomers.

The polymer obtained by polymerizing these acrylic cationic monomers has a high molecular weight and thus gives a resin of a high gel strength, in spite of the high water-absorptivity.

It is preferable that the water-absorptive resin of the present invention be capable to absorb pure water 10 to 500 times by weight as much as itself. Generally speaking, a resin having too high a water-absorptivity would have a low gel strength, while a resin having too low a water-absorptivity would cause the local concentration of a metabolite. In contrast to these resins, when the water-absorptive resin of the present invention is used as a carrier and absorbs water, the resulting cationic polymer gel has a low degree of crosslinking and thus various nutrients and waste matters can readily migrate therein.

0.01 to 1% by weight, based on the total monomers, of a crosslinking agent is required in order to achieve an appropriate water-absorptivity of the water-absorptive resin. The crosslinkage can be formed by copolymerizing the monomer(s) with a divinyl compound, post-crosslinking the same or combining these methods.

Examples of the divinyl compound to be copolymerized include N,N-methylenebisacrylamide and N-allylacrylamide.

Examples of the polyfunctional compound to be used in post-crosslinking include not only those capable of reacting with an amine, such as epichlorohydrin, diglycidylamine and diglycidyl ether, but also aldehydes capable of reacting with copolymerized acrylamide, such as formaldehyde.

When a divinyl compound is to be copolymerized with monomer(s), the whole monomers are dissolved in water and a water-soluble free-radical initiator is added to the resulting aqueous solution to thereby give a cationic water-absorptive resin. Spherical particles highly suitable as a carrier of a fluidized bed can be obtained by pearl polymerization, wherein an aqueous solution of monomers is dispersed in an oil and polymerized therein. The crosslinking density of the surface of the resin can be elevated by adding a polyfunctional compound such as diglycidyl ether to the oil. Post-crosslinking may be similarly carried out in the case where no divinyl compound is copolymerized. Alternately the post-crosslinking may be carried out by reacting the cationic polymer in a state of an aqueous solution with a polyfunctional compound.

Examples of the magnetic material to be incorporated in the cationic resin of a high water-absorptivity include particles such as beads, powders and granules of various ferrites and iron alloys. A magnetic

EP 0 304 143 A1

material of a poor corrosion resistance, for example, an iron alloy may be rendered rustproof by, for example, plating or treatment with silane (Si_nH_{2n+2}) .

It is preferable that the magnetic material be employed at a ratio by weight of 1:10 to 10:1, on a dry basis, based on the crosslinked polymer resin to be used in the present invention. When the ratio of the magnetic material to the resin exceeds the above range, the water-absorbing resin, i.e., the gel in the biodisposer can not be satisfactorily fluidized. On the other hand, the use of an excessively small amount of the magnetic material would make the recovery of the carrier difficult. It is further preferable that the carrier in a state of absorbing water should have a particle size of 0.5 to 20 mm.

The abovementioned gel, i.e., the water-absorbing resin, is generally fluidized by flowing air thereinto through a diffuser tube in the case of an aerobic fluidized bed, or by blowing methane gas thereinto in the case of an anaerobic one. It is also possible to fluidize the same by mechanical stirring. The water-absorbing resin in the form of a carrier on which a microorganism is fixed can be readily separated from the treated water by using a magnet and returned to the biodisposer.

Since the polymer gel to be used in the present invention for fixing a microorganism comprises cationic monomer(s) as the main constituting unit(s), the surface of the water-absorbing carrier, i.e., the gel is positively charged. Thus a microorganism, which is negatively charged in general, is adsorbed on the surface of the cationic gel to thereby form a dense microbial layer.

Nutrients for a microorganism, such as phosphate ion, which are anionic, would be concentrated within the gel and contribute to the growth of the microorganism.

Since the density of the crosslinking of this gel is low, various nutrients and waste matters can readily migrate therein.

The surface of the gel is continuously coated with a highly active microorganism, since the microbial layer adhereing to the surface of the gel is successively renewed. After the completion of the reaction, the magnetic gel can be readily recovered by using a magnet and returned to the biodisposer. Although the carrier can be readily separated from the treated water, the fluidization of the gel can be achieved by slightly stirring the same.

It is described in Japanese Patent Laid-Open No. 43203/1981 that a quaternary ammonium salt-type crosslinked polymer exerts a bactericidal effect. However the water-absorptive resin of the present invention would never exert such an effect. The following Examples are given by way of further illustration of the present invention.

Example:

35

20

(I) Synthesis Example 1

200 g of cyclohexane was introduced into a five-necked separable flask (500 ml) provided with a stirrer, a thermometer, a reflux condenser and a nitrogen inlet. 1 g of ethylcellulose (an ethyl derivative of cellulose) was added thereto and dissolved therein by heating the mixture to 60°C. Then nitrogen gas was blown into the flask to thereby replace oxygen with the same.

6 g of a triiron tetraoxide powder was dispersed in 75 g of an 80% aqueous solution of methacryloylox-yethyldimethylbenzylammonium chloride. 6.0 cc of a 10% aqueous solution of N,N-methylenebisacrylamide and 1.2 g of a 10% aqueous solution of 2,2-azobis(2-amidinopropane) hydrochloride were added thereto and the resulting mixture was introduced into a dropping funnel. Then nitrogen gas was passed thereth-rough to thereby replace oxygen with the same. The mixture was slowly added dropwise to the cyclohexane under stirring to thereby effect polymerization.

After carrying out the polymerization at 60°C for three hours, the reflux condenser was replaced with an azeotropic dehydrator and azeotropic dehydration was carried out within the flask in a water bath at 80 to 90°C under stirring. After thoroughly dehydrating, the polymer particles were filtered and the cyclohexane was removed by drying. Thus a highly water-absorptive resin was obtained in the form of beads.

These beads were screened to thereby select those having a particle size of 0.4 to 0.5 mm and the selected ones were allowed to absorb distilled water. Thus the crosslinked polymer absorbed water 35 times by weight as much as the polymer per se on a dry basis. This gel was referred to as G-1.

(II) Synthesis Example 2

125 g of an 80% aqueous solution of acryloyloxyethyltrimethylammonium chloride was introduced into a lidded glass container (300 ml) provided with a nitrogen inlet. 0.05 g of N,N-methylenebisacrylamide was dissolved therein and 100 g of triiron tetraoxide was dispersed therein. The resulting dispersion was heated to 60° C and purged with nitrogen. Then 3 ml of a 10% aqueous solution of 2,2′-azobis(2-amidinopropane) hydrochloride was added thereto and the obtained mixture was maintained at 60° C for five hours to thereby continue the polymerization. After the completion of the polymerization, the obtained mass was taken out, cut into a sheet of 5 mm in thickness and dried in a ventilated dryer at 100° C. The material thus dried was ground with a mill.

Then the ground material was screened to thereby select resin particles of 0.4 to 0.5 mm in particle size. The selected particles were allowed to absorb water. Thus this resin absorbed water 270 times by weight as much as the resin per se on a dry basis. This gel was referred to as G-2.

15

(III) Synthesis Example 3

10 g of a commercially available reagent-grade iron powder was introduced into a four-necked flask (300 ml) provided with a reflux condenser, a nitrogen inlet and a stirrer. 100 ml of xylene and 0.3 g of acryloyloxypropyltrimethoxysilane were added thereto and the resulting mixture was allowed to react at 60°C for 18 hours. Then 30 g of hydroxyethyl acrylate was added thereto and the mixture was purged with nitrogen. 0.1 g of azobisisobutyronitrile was further added thereto and the polymerization was continued at 60°C for six hours. The solid matters were filtered, washed and dried. The solid product thus obtained was ground and dispersed in 75 g of an 80% solution of a reaction product between N,N-dimethylaminopropylacrylamide and methyl chloride in which 0.02 g of methylenebisacrylamide was dissolved. Subsequently 1.8 ml of a 10% aqueous solution of 2,2 -azobis(2-amidinopropane) hydrochloride was added thereto, similar to the above Synthesis Example 1, and polymerization was effected at 60°C for five hours. The obtained product was dried and ground to thereby give a magnetic, water-absorptive resin. This resin, which had a water-absorption capacity of 90-fold, was referred to as G-3.

30

(IV) Synthesis Example 4

2 g of N,N-dimethylaminopropylacrylamide and 18 g of acrylamide were introduced into a lidded glass container (300 ml) provided with a nitrogen inlet. These compounds were then dissolved in 180 ml of deionized water and the pH value of the solution was adjusted to 4.5 with sulfuric acid. After subjecting the solution to nitrogen purging, 0.2 ml of a 1% aqueous solution of ammonium persulfate and 0.2 ml of a 1% aqueous solution of sodium hydrogen sulfite were added thereto to thereby effect polymerization. Five hours thereafter, 20 g of a triiron tetraoxide powder and 20 ml of formalin diluted 100-fold were added to the polymer solution and thoroughly mixed therewith. Then the mixture was transferred into a Petri dish of 15 cm in diameter and dried in a ventilated drier at 110 °C. The dried matter was ground with a mill and screened to thereby select resin particles having a particle size of 0.4 to 0.5 mm. The selected particles were allowed to absorb distilled water. Thus the crosslinked polymer absorbed water 30 times by weight as much as the polymer per se on a dry basis. This gel was referred to as G-4.

45

(I) Comparative Synthesis Example 1

300 g of a 30% aqueous solution of acrylamide was introduced into a lidded glass container (500 ml) provided with a nitrogen inlet. 0.05 g of N,N-methylenebisacrylamide was dissolved therein and 90 g of triiron tetraoxide was dispersed therein. The resulting dispersion was subjected to nitrogen purging and 1 ml of a 1% aqueous solution of ammonium persulfate and 1 ml of a 1% aqueous solution of sodium hydrogen sulfite were added thereto at 20°C to thereby effect polymerization. After the completion of the polymerization, the obtained mass was taken out, cut into a sheet of 5 mm in thickness, dried in a ventilated drier at 100°C and ground with a mill. Then the material was screened to thereby select resin particles having a particle size of 0.4 to 0.5 mm. The resin thus selected was allowed to absorb distilled water. As a result, this crosslinked polymer abosrbed water 40 times by weight as much as the polymer per se on a dry basis. This gel was referred to as G-5.

(II) Comparative Synthesis Example 2

1.5 g of a triiron tetraoxide powder was dispersed in 100 ml of a 3% aqueous solution of agarose in the form of a sol at 45°C. The resulting dispersion was molded into beads of 4 to 5 mm in particle size and cooled to thereby give a gel. This gel was referred to as G-6.

(I) Example 1

Surplus sludge of sewage (sludge concentration: 4000ppm) was introduced into an aerator (20 t) provided with a diffuser tube at the bottom and air was blown thereinto at a rate of 20 t.min. The water-absorptive resin prepared in each Synthesis Example as described above was added thereto as a carrier in an amount of 100 g (including the magnetic material) on a dry basis. Then an artificial waste water of the following composition was supplied to the aerator at a constant rate. The carrier absorbing water, i.e., the gel in the effluent from the aerator was recovered by using a magnet and returned to the aerator. This treatment was continuously carried out for 30 days at 25 °C. Table 1 shows the properties of the water thus treated.

Composition of artificial waste water:

oxidized starch: 250 ppm, peptone: 250 ppm,

KH₂PO₄: 15 ppm and BOD: 390 ppm.

Table 1

Result of aerobic biological treatment					
	Sample	BOD load (kg/m³•day)	BOD of treated filtrate (ppm)		
Example	G-1	4.5	5		
	G-2	6.5	11		
	G-3	5.5	7		
	G-4	4.0	9		
Comp.	G-5	1.0	390		
Example	G-6	1.0	390		

35

40

25

30

(II) Example 2

The content of a septic tank for human waste and 100 g (including the magnetic material; on a dry basis) of the water-absorptive resin prepared in each Synthetic Example as described above were introduced into a hermetically closed septic tank (20 t) provided with a gas chamber (10 t) at the top and a circulating diffuser tube for blowing the gas from the gas chamber into the bottom. Then an artificial waste water of the following composition was supplied to the septic tank at a constant rate.

The gas chamber was filled with methane gas and the circulation/aeration was continued. The resin absorbing water, i.e., the gel contained in the effluent from the tank was recovered by using a magnet and returned to the tank. This treatment was continued at 45 °C for 30 days. Table 2 shows the properties of the water thus treated.

Composition of artificial waste water:

glucose: 2000 ppm, urea: 200 ppm,

(NH₄)₂HPO₄: 20 ppm and BOD: 1400 ppm.

55

Table 2

Result of anaerobic biological treatment						
	Sample	BOD load (kg/m³ • day)	BOD of treated filtrate (ppm)			
Example	G-1	6.0	230			
	G-2	7.5	210			
	G-3	7.0	190			
	G-4	6.0	280			
Comp.	G-5	1.0	1300			
Example	G-6	1.0	. 1350			

15

5

10

Claims

1. A water-absorptive resin for a microbial carrier in a fluidized bed biodisposer, which comprises a magnetic material incorporated in a cationic crosslinked polymer comprising at least 10% by weight of cationic monomer unit(s) of the following formula:

25

20

$$-CH_{2} \xrightarrow{\stackrel{R}{\downarrow} 1} {\stackrel{R}{\downarrow} 2} {\stackrel{R}{\downarrow} 2} {\stackrel{C}{\downarrow} -A-B-N} \xrightarrow{-R_{4}} {\stackrel{\Theta}{\downarrow}} {\stackrel{\Theta}{\downarrow}}$$

$$\stackrel{R}{\downarrow} {\stackrel{R}{\downarrow} 1} {\stackrel{R}{\downarrow} 2} {\stackrel{R}{\downarrow}$$

30

45

wherein A represents an oxygen atom or an NH group,

B represents a C₂H₄, C₃H₆ or CH₂CH(OH)CH₂ group,

R₁ represents a hydrogen atom or a methyl group,

R2 and R3, which may be the same or different, each independently represent a methyl or ethyl group,

R₄ represents a hydrogen atom or a methyl, ethyl, benzyl or 3-chloro-2-hydroxypropyl group, and

X⁻ represents an anion.

- 2. A water-absorptive resin according to claim 1, wherein said cationic crosslinked polymer absorbs water at least ten times as much as the polymer per se on a dry basis.
- 3. A water-absorptive resin according to claim 1 or 2, which serves as a microbial carrier in a fluidized bed in a state of absorbing water.
- 4. A water-absorptive resin according to claim 1, 2 or 3, wherein said cationic monomer(s) are selected from tertiary amines and quaternary ammonium salts of dialkylaminoalkyl (meth)acrylate and dialkylaminoalkyl (meth)acrylamide.
- 5. A water-absorptive resin according to any one of the preceding claims, wherein in the cationic monomer unit of formula (I), R_1 is a methyl group, R_2 and R_3 are each a methyl group, R_4 is a benzyl group, A is an oxygen atom and B is a C_2H_4 group.
- 6. A water-absorptive resin according to any one of claims 1 to 4, wherein in the cationic monomer unit of formula (I), R_1 is a hydrogen atom, R_2 , R_3 and R_4 are each a methyl group, A is an oxygen atom and B is a C_2H_4 group.
- 7. A water-absorptive resin according to any one of claims 1 to 4, wherein in the cationic monomer unit of formula (I), R_1 is a hydrogen atom, R_2 , R_3 and R_4 are each a methyl group, A is an NH group and B is a C_3H_6 group.
- 8. A water-absorptive resin according to any one of the preceding claims, which comprises 90% by weight or less of monomer unit(s) selected from ethylenically unsaturated carboxylic acids, esters thereof and amides thereof.

EP 0 304 143 A1

- 9. A water-absorptive resin according to claim 8, which comprises 90% by weight or less of (meth)-acrylamide monomer unit(s).
- 10. A water-absorptive resin according to any one of the preceding claims, said resin being obtained by polymerisation of the said monomer or monomers in the presence of 0.01 to 1% by weight, based on the whole monomers, of a crosslinking agent.
- 11. A water-absorptive resin according to claim 10, wherein said crosslinking agent is N,N-methylenebisacrylamide or N-allylacrylamide, or a mixture thereof.
- 12. A water-absorptive resin according to claim 10, wherein a polyfunctional compound is used as said crosslinking agent.
- 13. A water-absorptive resin according to claim 10, wherein the crosslinking agent is selected from epichlorohydrin, diglycidylamine, diglycidyl ether and formaldehyde.
- 14. A water-absorptive resin according to any one of the preceding claims, wherein the resin is a resin which has been obtained by dispersing an aqueous solution of monomer(s) in an oil and pearl-polymerizing the same.
- 15. A water-absorptive resin according to any one of the preceding claims, wherein the weight ratio of the magnetic material to the crosslinked polymer on a dry basis, ranges from 1:10 to 10:1.
- 16. A water-absorptive resin according to any one of the preceding claims, wherein said magnetic material is a ferrite such as magnetite or triiron tetraoxide (Fe₃ O₄) in the form of particles such as beads, powders or granules.
- 17. A water-absorptive resin according to any one of claims 1 to 16, wherein said magnetic material is an iron alloy in the form of particles such as beads, powders or granules.
- 18. A water-absorptive resin according to claim 17, wherein said magnetic material is an iron alloy rendered rustproof by, for example, plating or treatment with silane.
- 19. A water-absorptive resin according to claim 18, wherein said magnetic material is obtained by absorbing acryloyloxypropyltrimethoxysilane on the surface of the magnetic metal and polymerizing the silane to thereby render said magnetic metal rustproof.
- 20. A water-absorptive resin according to any one of the preceding claims, wherein said carrier in a state of absorbing water can be recovered by using a magent.
- 21. A water-absorptive resin according to any one of the preceding claims, wherein the specific gravity of said carrier in a state of absorbing water is closely similar to that of the water to be treated in an aerator.
- 22. A water-absorptive resin according to any one of claims 1 to 20, wherein the specific gravity of said carrier in a state of absorbing water is closely similar to that of the water to be treated in a septic tank.
- 23. A water-absorptive resin according to any one of the preceding claims, wherein said carrier in a state of absorbing water has a particle size of 0.5 to 20 mm.

35

30

10

15

20

45

40

50

5**5**

EUROPEAN SEARCH REPORT

88 30 3631

		•		EP 00 30 3	
	DOCUMENTS CONSII	DERED TO BE RELEVA	ANT		
Category	Citation of document with income of relevant pass		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)	
Y	US-A-3 926 756 (A.J * Claim 1, abstract	. RESTAINO)	1,4-6,8 ,9,16, 17,20	C 02 F 3/10 C 12 N 11/08 C 08 F 20/60	
Y	EP-A-0 209 790 (BAY * Claims 1,2,8 *	ER AG)	1,4-6,8 ,9,16, 17,20	C 08 F 20/34 C 08 L 33/14	
Α	WO-A-8 100 575 (BEF * Claims 1,2,9,10; p		1,15-18 ,20		
A	BIOTECHNOLOGY AND BI 23, no. 11, November 2561-2567, John Wile York, US; EIZO SADA "Performance of flui utilizing magnetic f * Page 2561, line 1 11 *	1981, pages by & Sons, Inc., New et al.: dized-bed reactors fields"	1,3,11, 16,20		
				TECHNICAL FIELDS	
				SEARCHED (Int. Cl.4)	
				C 02 F C 12 N C 12 M C 08 K C 08 L	
		·		·	
	The present search report has b	een drawn up for all claims			
T11	Place of search E HAGUE	Date of completion of the searce 07-10-1988	1	Examiner ILLARD P.J.H.M.	
X:pa Y:pa do A:te O:ne	CATEGORY OF CITED DOCUMENT CATEGORY OF CITED DOCUMENT COMPANY TO THE PROPERTY OF CATEGORY COMPANY THE ACCUMENT OF THE PROPERTY OF CATEGORY	NTS T: theory or p E: carlier pate after the fi ther D: document L: document	orinciple underlying the ent document, but pub illing date cited in the applicatio cited for other reasons	e invention lished on, or n	

EPO FORM 1503

THIS PAGE BLANK (USPTO)